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## Evolution of Iron speciation during hydration of C<sub>4</sub>AF.

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### Abstract

Although the calcium silicate and calcium aluminate phases are good candidates for metal retention in real cement, the role of the calcium-ferric aluminate phase, shorthand C<sub>4</sub>AF, should not be neglected. Indeed, sorption isotherms indicated that all metals showed a strong affinity for the hydration products of C<sub>4</sub>AF. The C<sub>4</sub>AF content in Portland cement is 2-7% and the Fe<sub>2</sub>O<sub>3</sub> content is in the 1 to 3,5% range. It is therefore reasonable to assume that a non negligible proportion of the trace metals in an actual cement will be associated with Fe phases. However, the metal retention capabilities of those phases have received little attention.

Previous investigations have shown that the minerals formed during the hydration of  $C_4AF$  are similar to those formed from  $C_3A$  (pure tri calcium aluminate) under comparable conditions. Nevertheless no investigation was conducted at the molecular level and there is still a controversy whether Fe substitutes for Al in the hydrated minerals in whole or in part, or if it forms  $FeOOH$  clusters scattered throughout the matrix.

In this context we have conducted XAS experiments at the LURE and ELETTRA synchrotrons. It was found that the hydration of  $C_4AF$  leads to the formation of  $C_3AH_6$  (hydrogarnet) in which Fe randomly substitutes for Al in the  $C_3AH_6$  structure, and also forms an amorphous  $FeOOH$  phase. Intermediate products like AFm (i.e. an ill organized lamellar phase) are also formed but they rapidly evolved to  $C_3AH_6$  and iron does not seem to be incorporated in the AFm structure.

Key words:

Ferro-calcium aluminate, iron oxyhydroxides, EXAFS, heavy metal fixation.

## INTRODUCTION

Although the calcium silicate and calcium aluminate phases are good candidates for metal retention in real cement, the role of the ferro-calcium aluminate phase ( $C_4AF$ ) should not be neglected. Indeed, sorption isotherms indicated that all metals showed a strong affinity for the hydrated  $C_4AF$  phase (Moulin, 1999)). The ferro-calcium aluminate content in Portland cement is 2-7% and the  $Fe_2O_3$  content is in the 1 to 3,5% range. It is therefore reasonable to assume that a non negligible proportion of the trace metals in an actual cement will be associated with Fe phases. However, the metal retention capabilities of those phases (either isolated or within a cement) have received only little attention. Moreover the accurate speciation of iron in cement is not fully determined. Many investigations have shown that the minerals formed during the hydration of  $C_4AF$  are essentially similar to those formed from tri-calcium aluminate ( $C_3A$ ) under comparable conditions (Chatterji and Jeffrey (1962), Carlson (1964), Collepardi et al. (1979), De Keyser and Tenoutasse, (1969), Schwiete and Iwai (1964), Emanuelson and Hansen, 1997, Meller et al. (2004)). The first minerals formed in the absence or presence of  $CaSO_4$  are the ill organized lamellar phases AFm and AFt respectively. Both types of phases contain  $Al^{3+}$  and  $Fe^{3+}$  and tend to undergo further changes to form hydrogarnet phases. Moreover Teoreanu et al. (1979), Fukuhara et al. (1981), Rogers and Aldrige (1977), and Brown (1987) indicated the possible formation of an amorphous  $FeOOH$  phase.

Nevertheless no investigation was conducted at the molecular level and a controversy still exists: does all the Fe substitute for Al or are there FeOOH clusters embedded in the formed hydrated minerals?

The aim of our work was to monitor the evolution of iron speciation during the hydration of C<sub>4</sub>AF in lime water. The structure of iron at the atomic scale has been investigated using X-ray Absorption Spectroscopy.

## Material and methods.

### C<sub>4</sub>AF hydration:

Starting materials consisted of an anhydrous ferrite (Brownmillerite) C<sub>4</sub>AF obtained from Lafarge Ciments (Vivier, France) hydrated with lime water (LW) with a water/ solid ratio of 10 and 0.5 on a rotary shaker and filtered (0.2 µm). The recovered solid was dried with acetone. The C<sub>4</sub>AF were hydrated during 24, 48 hours and 7 days.

### X-ray Diffraction.

Solids from the sound core and the leached layer were mechanically separated, ground to fine powder, and analyzed by X-ray diffraction. A PhilipsPW3710 X-ray diffractometer with a Co K $\alpha$  radiation at 40 kV and 40 mA was used. The diffractograms were scanned in the 2 $\theta$  3.5-78° range with a counting time of 12 s per 0.02° step.

### Electron Microscopy

SEM-EDX images and elemental analysis were obtained using a Phillips XL30 SFEGSEM coupled to an Oxford Instruments energy dispersive spectrometer (EDS). The SEM was operated at 20 keV.

### X-ray Absorption Spectroscopy.

X-ray absorption spectroscopy (XAS) experiments were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE, Paris-France) on the D44 beamline

and at the ELLETRA synchrotron facility on the BL 11.1 beamline. The Si(111) monochromator crystals were used to scan energy from 100 eV below to 800 eV above the Fe K-edge. The samples were measured in the transmission mode.

EXAFS data reduction was accomplished according to a procedure described previously (Manceau and Calas, 1986). The Fourier transform yields radial distribution functions (RDF) consisting of  $n$  peaks representing  $n$  coordination spheres at  $R_n$  distances from the central atom. Distances are uncorrected for phase shift and have to be displaced toward long distances by 0.3–0.4 Å from the crystallographic position. The structural and chemical parameters  $R_j$ ,  $N_j$  ( $N$ : number of atoms) and nature of atomic neighbors in the  $j^{\text{th}}$  shell around Fe were determined by least-squares fitting of partial EXAFS spectra. The uncertainties on  $R$  and  $N$  are 0.06 Å and 10%, respectively.

## Results and Discussion:

### Hydration kinetics of C<sub>4</sub>AF

The key point to study the reactivity of the C<sub>4</sub>AF mineral phase in cement is to determine the dissolution kinetics of the anhydrous mineral. In order to characterize the effect of the pH, hydration experiments were performed at various liquid/solid ratio and hydration pHs (lime water, pH=11, 10 and 9 with NaOH). The figure 1-A presents the XRD pattern of C<sub>4</sub>AF hydrated during 48 hours with a liquid/solid ratio of 10. The different peaks shown in figure 1-A correspond to anhydrous C<sub>4</sub>AF and hydrogarnet (C<sub>3</sub>AH<sub>6</sub>). After 48 hours of hydration with a Liquid/Solid ratio =10, almost all the anhydrous C<sub>4</sub>AF has been dissolved. The C<sub>3</sub>AH<sub>6</sub> XRD peak intensities are slightly higher at pH = 10 than at pH = 9 and lime water indicating that the formation of C<sub>3</sub>AH<sub>6</sub> is faster, or the crystallinity of the hydrogarnet is better, at pH= 10 than in lime water. However it should be noted that in the present case the relevant parameter is not the pH but the Ca concentration. Scrivener and Pratt (1984) indicated that

lime water delays the  $C_4AF$  hydration, presumably because of the sorption of calcium at the surface of  $C_4AF$  thus creating a barrier to water. After 7 days of hydration with a  $L/S = 0.5$  the various samples exhibit the same diffraction patterns except for a broad peak at  $13.5^\circ$  ( $7.59\text{\AA}$ ) that is present only for three samples ( $C_4AF$   $L/S = 0.5$  after 7 days hydrated with lime water,  $NaOH$   $pH=9$  and  $11$ ). This very small and broad peak corresponds to Afm phases such as  $C_3A.CaCO_3.11H_2O$  ( $7.56\text{\AA}$ ). Indeed, this mineral is a temporary phase that appears during the first hydration stages (after 24 h of hydration) as shown in figure 1-B. In the case of pure  $C_4AF$  system, water and carbonate molecules occupy the inter-layer site. These Afm phases are clearly identified after 24 hours as seen in figure 1-C. During the hydration processes and in the absence of calcium sulfate Afm minerals evolve into hydrogarnet phases.

Therefore the hydration of  $C_4AF$  leads to the formation of hydrogarnet regardless of the pH of hydration. After 7 days, some Afm phases still exist but no crystallised iron oxide or hydroxide phases have been detected. For a more in-depth investigation, EXAFS spectroscopy has been used to determine the atomic environment of iron. This technique provides complementary information to XRD since amorphous phases are also observed by EXAFS.

### Iron speciation

The analysis and modelling of EXAFS spectra enable the identification of the atomic environment of the target atom, i.e. iron in our case. The very interesting point is that EXAFS is sensitive to modifications of the crystallinity and mineralogy of Fe phases. Moreover EXAFS accurately characterizes the atomic structure of amorphous phases. From XRD we know that Afm and  $C_3AH_6$  exist in the samples. The question is to know whether or not Fe can replace Al in the hydrogarnet and Afm structures and if other Fe phases are present.

Figure 2 displays the pseudo-radial distribution function (PRDF) of the C<sub>4</sub>AF hydrated during 1 week and is compared to the PRDFs of Fe-garnet, and two iron oxy-hydroxides (goethite and lepidocrocite). The various peaks of the PDRF correspond to the probability to find atoms around the central atom (Fe) at the distance (R) of the peaks. In the case of iron the first peak correspond to the presence of oxygen atoms with a Fe-O interatomic distance  $\approx 2$  Å. The second peak corresponds to atoms in the next nearest coordination spheres. The differences in position and amplitude suggest that the atomic environment of Fe is different in the sample and in the reference compounds, i.e. no pure Fe-garnet or oxy-hydroxides are formed.

The modelling of the first peak indicates that each iron is surrounded by 6 oxygen atoms at 2 Å. Therefore each iron is at the center of an octahedron formed by 6 surrounding oxygen atoms.

The results of the modeling of the second peak are presented in table 1. These results indicate that each iron is surrounded by  $2.1 \pm 0.4$  Fe atom atoms at  $3.03 \pm 0.02$  Å,  $0.2 \pm 0.05$  Fe atoms at  $3.45 \pm 0.02$  Å and  $2.1 \pm 0.4$  calcium atoms at  $3.59 \pm 0.02$  Å. The interpretation of EXAFS structural results requires the comparison with atomic structure of reference compounds. Table 2 presents the atomic structure of different reference compounds and figure 3 illustrates the corresponding structures of Fe at the molecular scale. The comparison between structural results obtained in the case of C<sub>4</sub>AF hydrated during 1 week and the structural data of reference compounds suggests that the Fe--Fe interatomic distances determined for the hydrated C<sub>4</sub>AF are similar to those of goethite and amorphous FeOOH. From the 3D structure it is possible to determine the type of linkage between Fe octahedra corresponding to Fe--Fe interatomic distances of 3.03 and 3.45 Å. The short Fe--Fe distance corresponds to edge sharing between Fe octahedra and the longer one corresponds to double corner linkages as illustrated in figure 4. The fact that Fe octahedra are linked mainly through



edge indicates that Fe hydroxide or oxy-hydroxides exist in the sample. If Fe was only present in the hydrogarnet or AFm, no Fe--Fe contribution would have been detected. The Fe--Ca atomic pair determined in the hydrated C<sub>4</sub>AF corresponds to the hydrogarnet structure and not to the AFm phase. Indeed the Fe--Ca interatomic distance in the AFm is 3.35 Å and 3.51 Å in the case of hydrogarnet, which is what has been determined for our hydrated sample.

In the case of the C<sub>4</sub>AF hydrated during 24 hours, XRD analysis indicate that AFm phases are formed. EXAFS results indicate that no Fe—Ca interaction exist, thus suggesting that Fe is not associated with AFm phases and that amorphous FeOOH phases are formed.

Therefore it appears that the hydration leads to the formation of hydrogarnet in which Fe can replace Al, and the additional formation of Fe amorphous oxy-hydroxides. SEM-EDX results have also demonstrated that under our experimental conditions iron is not associated to the AFM phases (figure 5).

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*Table 1: structural results of the analysis of the second coordination sphere of Fe in C4AF hydrated during 24 hours and 1 week.*

Sample	Atomic pair	R(Å)	$\sigma$ (Å)	N	Residue
C4AF	Fe—Fe	3.03	0.111	3.1	0.012
24h	Fe—Fe	3.46	0.093	1.3	
C4AF	Fe—Fe	3.03	0.104	2.1	0.0389
1 week	Fe—Fe	3.45	0.070	0.2	
	Fe—Ca	3.59	0.091	2.1	

Table 2: iron atomic environment of different reference compounds

<i>Mineral</i>	<i>Atomic pair</i>	<i>Distance (Å)</i>	<i>Number</i>	<i>Reference</i>
<i>Goethite</i> (□-FeOOH)	<i>Fe-O</i>	<i>1.95</i>	<i>3</i>	<i>Szytula et al. (1968)</i>
	<i>Fe-O</i>	<i>2.09</i>	<i>3</i>	
	<i>Fe--Fe</i>	<i>3.01</i>	<i>2</i>	
	<i>Fe--Fe</i>	<i>3.28</i>	<i>2</i>	
	<i>Fe--Fe</i>	<i>3.46</i>	<i>4</i>	
<i>Ferrihydrite</i> (amorphous-FeOOH)	<i>Fe--Fe</i>	<i>3.01</i>	<i>4.5</i>	<i>Manceau et al. 1993</i>
	<i>Fe--Fe</i>	<i>3.43</i>	<i>3.9</i>	
<i>Hemathite</i> (□-Fe <sub>2</sub> O <sub>3</sub> )	<i>Fe-O</i>	<i>1.94</i>	<i>3</i>	<i>Blacke R.Z., et al.(1966)</i>
	<i>Fe-O</i>	<i>2.11</i>	<i>3</i>	
	<i>Fe--Fe</i>	<i>2.90</i>	<i>1</i>	
	<i>Fe--Fe</i>	<i>2.97</i>	<i>3</i>	
	<i>Fe--Fe</i>	<i>3.36</i>	<i>3</i>	
	<i>Fe--Fe</i>	<i>3.70</i>	<i>6</i>	
<i>Andradite Fe-garnet</i>	<i>Fe-O</i>	<i>2.02</i>	<i>6</i>	<i>Hazen and Finger (1989)</i>
	<i>Fe--Ca</i>	<i>3.36</i>	<i>6</i>	
	<i>Fe--Si</i>	<i>3.36</i>	<i>6</i>	
<i>Hydrogarnet</i> <i>C<sub>3</sub>(A/F)H<sub>6</sub></i>	<i>Al/Fe-O</i>	<i>1.91</i>	<i>6</i>	<i>Lager &amp; Von Dreele (1996)</i>
	<i>Al/Fe--Ca</i>	<i>3.51</i>	<i>6</i>	
<i>AFm</i>	<i>Al/Fe-O</i>	<i>1.90</i>	<i>6</i>	
	<i>Al/Fe--Ca</i>	<i>3.35</i>	<i>5</i>	

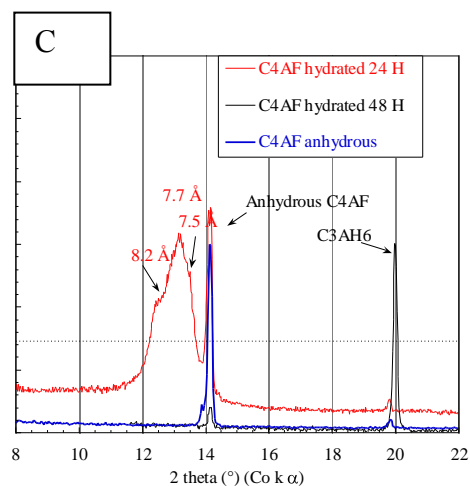
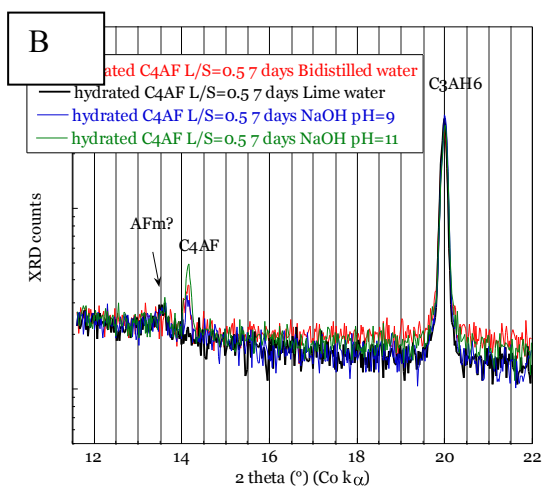
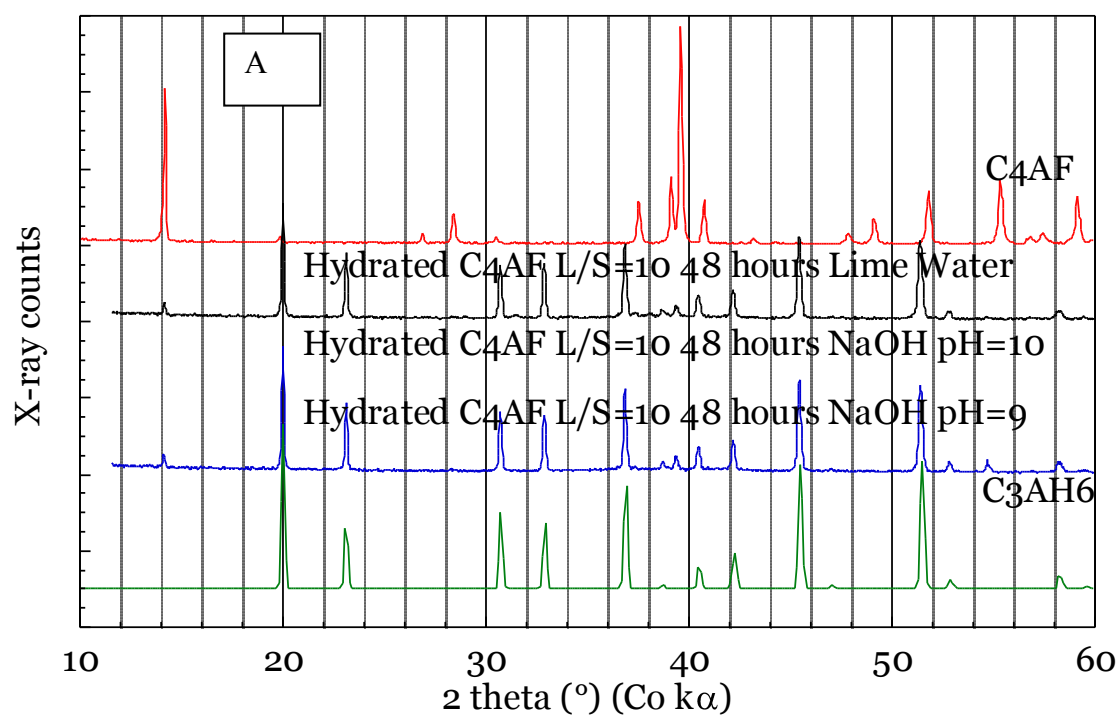


Figure 1: A) XRD pattern of anhydrous C<sub>4</sub>AF, C<sub>3</sub>AH<sub>6</sub> and various hydrated C<sub>4</sub>AF after 48 Hours, B) Zoom of the 12-22 ° area. C) XRD pattern of C<sub>4</sub>AF hydrated after 24 and 48 Hours.

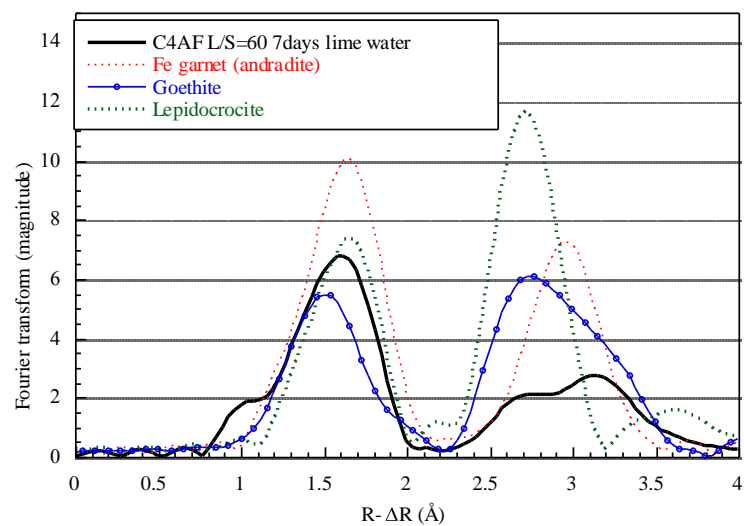


Figure 2: Pseudo-radial distribution functions of C4AF hydrated during 1 week and three reference compounds: Fe-garnet and two iron oxy-hydroxides goethite and lepidocrocite.

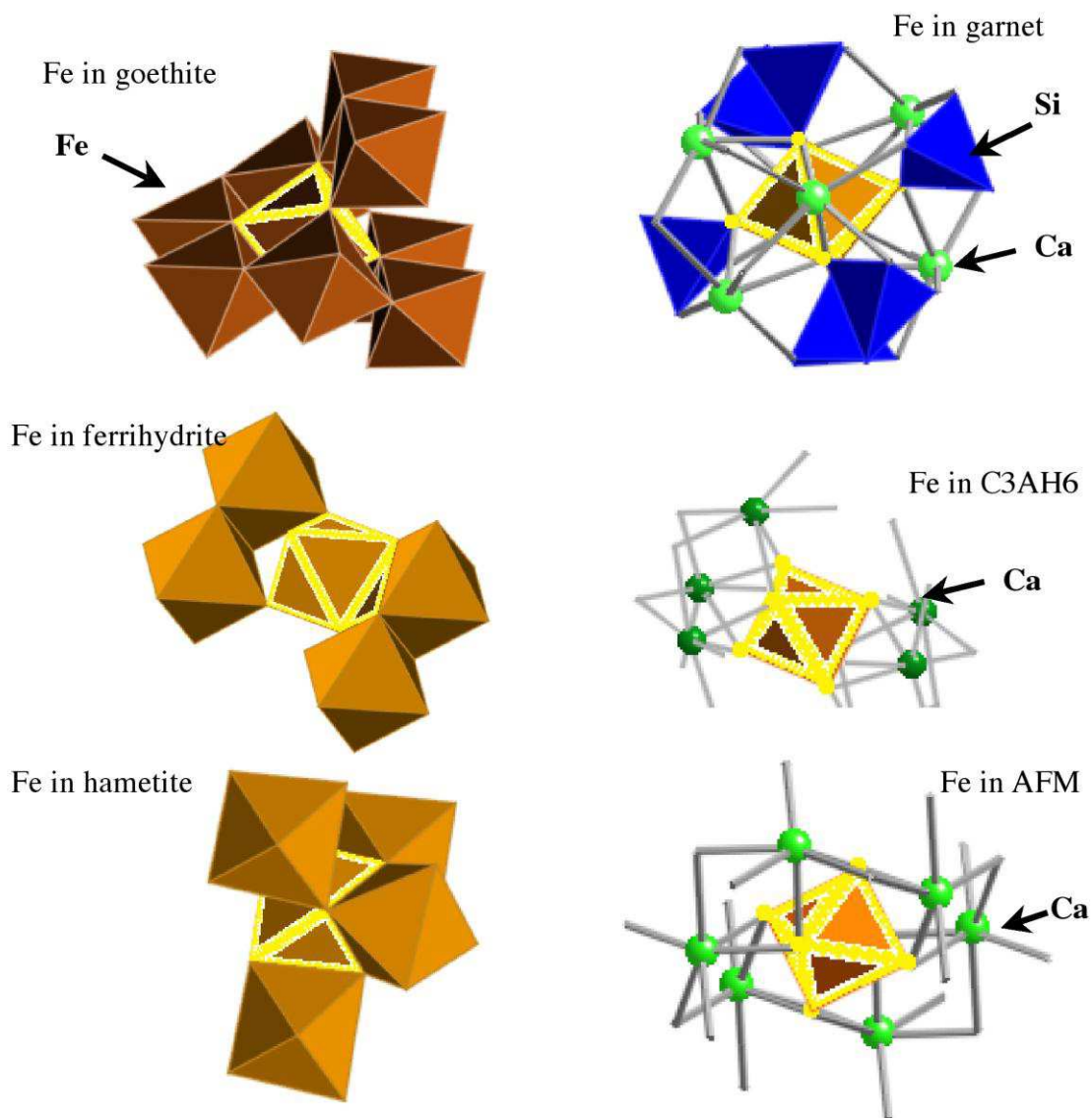


Figure 3: atomic environment around Fe in different Fe minerals. These differences in term of structure lead to different interatomic distances as shown in table 2.

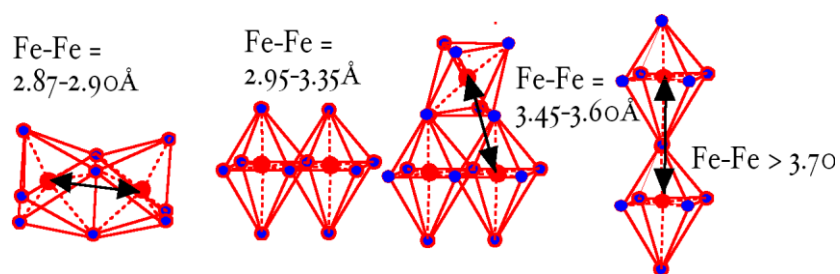
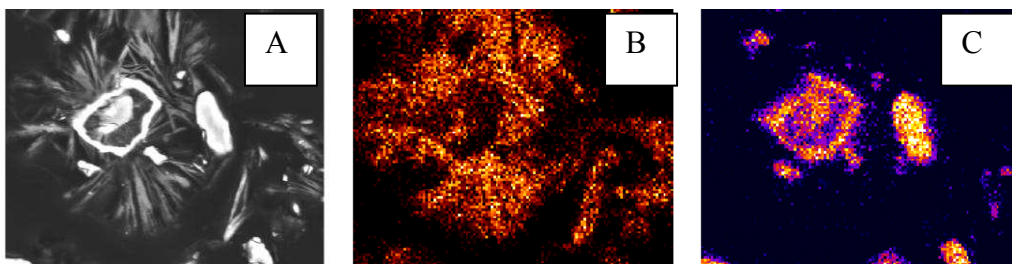


Figure 4: Face, edge ( $2.97\text{\AA} < \text{Fe}-\text{Fe} < 3.36\text{\AA}$ ) and double corner ( $3.40\text{\AA} < \text{Fe}-\text{Fe} < 3.66\text{\AA}$ ) sharing between Fe octahedra.



**Figure 5: SEM-EDX image of C4AF hydrated during 24 hours A) Backscattered electron image B) Al image C) Fe image.**